

(12) **UK Patent Application** (19) **GB** (11) **2 270 687** (13) **A**

(43) Date of A Publication 23.03.1994

(21) Application No 9319405.8

(22) Date of Filing 20.09.1993

(30) Priority Data

(31) 04250863 (32) 21.09.1992 (33) JP
05071123 04.03.1993

(71) Applicant(s)

Matsushita Electric Works Ltd

(Incorporated in Japan)

1048, Oaza-Kadoma, Kadoma-shi, Osaka 571, Japan

Koichi Niihara

**1142 Kori-Godo-Shukusha, 9-7 Korigaoka,
Hirakata-Shi, Osaka, Japan**

(72) Inventor(s)

Keiichi Yamazaki

Masahiro Nawa

Koichi Niihara

Atsushi Nakahira

Tohru Sekino

(51) INT CL⁵

C04B 35/48 , C22C 29/12 32/00

(52) UK CL (Edition M)

**C1J JX J1 J11 J19 J2 J21 J33 J4 J7 J9
C7A AA249 AA25X AA25Y AA250 AA253 AA255 AA257
AA259 AA260 AA263 AA266 AA269 AA27X AA272
AA276 AA279 AA299 AA30X AA30Y AA300 AA303
AA305 AA307 AA309 AA31X AA311 AA313 AA316
AA319 AA320 AA323 AA326 AA329 AA33X AA33Y
AA330 AA335 AA337 AA339 AA34X AA34Y AA340
AA341 AA343 AA345 AA347 AA349**

(52) (56) and (58) continued overleaf

(74) Agent and/or Address for Service

Beresford & Co

**2-5 Warwick Court, High Holborn, LONDON,
WC1R 5DJ, United Kingdom**

(54) **Zirconia based composite material**

(57) A zirconia based composite material includes partially stabilized zirconia including 1.5 to 4.5 mol% of yttrium oxide as matrix and a phase of at least one metal selected from titanium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten as metal grains dispersed in the matrix. The metal phase has a melting point higher than a sintering temperature of the zirconia. The composite material may further contain a phase of at least one ceramic selected from Al_2O_3 , SiC, Si_3N_4 , B_4C , carbides, nitrides and borides of titanium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten as ceramic grains dispersed in the matrix. The composite material may be manufactured by preparing a mixture incorporating at least one first constituent forming the partially stabilized zirconia and at least one second constituent forming the metal phase, and if necessary, at least one third constituent forming the ceramic phase and sintering the mixture in a non-oxidation atmosphere.

GB 2 270 687 A

AA369 AA37X AA37Y AA370 AA375 AA377 AA379
AA38X AA381 AA383 AA385 AA387 AA389 AA39X
AA39Y AA390 AA394 AA396 AA398 AA40Y AA400
AA402 AA404 AA406 AA409 AA41X AA41Y AA410
AA414 AA416 AA418 AA42X AA422 AA425 AA428
AA43X AA432 AA435 AA437 AA439 AA44Y AA440
AA447 AA449 AA45X AA451 AA453 AA455 AA457
AA46X AA46Y AA461 AA463 AA465 AA467 AA469
AA47X AA471 AA473 AA475 AA477 AA479 AA48X
AA481 AA483 AA485 AA487 AA489 AA49X
AA491 AA493 AA495 AA497 AA499 AA50X
AA501 AA503 AA505 AA507 AA509 AA51X AA51Y
AA514 AA517 AA519 AA52X AA521 AA523 AA525
AA527 AA529 AA53X AA53Y AA531 AA533 AA535
AA537 AA539 AA54X AA541 AA543 AA545 AA547
AA549 AA579 AA599 AA60X AA60Y AA600 AA601
AA603 AA605 AA607 AA609 AA61X AA61Y AA613
AA615 AA617 AA619 AA62X AA621 AA623 AA625
AA627 AA629 AA67X AA671 AA673 AA675 AA677
AA679 AA68X AA681 AA683 AA685 AA686 AA689
AA69X AA693 AA694 AA697 AA699 AA70X A71X
A71Y

(56) Documents Cited

GB 1295413 A GB 1109368 A GB 1105646 A

(58) Field of Search

UK CL (Edition L) C1J , C7A

INT CL⁵ C04B 35/00 35/48 , C22C 29/00 29/12 32/00

ONLINE DATABASE: WPI

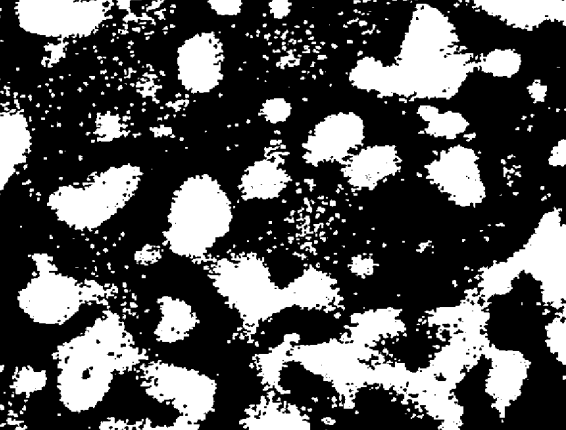
A high-magnification micrograph showing a surface with a granular, textured appearance. The surface is covered with numerous small, bright, irregularly shaped features, possibly pores or particles, set against a darker, more uniform background. In the bottom right corner, there is a scale bar consisting of a horizontal line with the text "23 μm" above it.

FIG.2

212



FIG.3

SPECIFICATION

ZIRCONIA BASED COMPOSITE MATERIAL AND METHOD OF
MANUFACTURING THE SAME PRODUCT

5 TECHNICAL FIELD

The present invention is directed to a zirconia based composite material having excellent mechanical strength and toughness, and also a method of manufacturing the same product.

10 BACKGROUND ART

A partially stabilized zirconia, which is formed by addition of a preferable amount of a stabilizer such as yttrium oxide (Y_2O_3), cerium oxide (CeO_2), or magnesium oxide (MgO), etc., to zirconia (ZrO_2), has been well known as a
15 ceramic material having higher mechanical strength and toughness than another popular ceramic materials such as aluminum oxide (Al_2O_3), silicon carbide (SiC), or silicon nitride (Si_3N_4), etc. The partially stabilized zirconia possesses an unique mechanism for improving the toughness
20 thereof. That is, a metastable tetragonal zirconia phase in the partially stabilized zirconia is transformed to a stable monoclinic zirconia phase under a stress concentration occurring at a crack tip in the zirconia. Since the transformation, which is generally called as a stress induced
25 phase transformation, is accompanied with a volume expansion of zirconia, a progress of the crack is effectively prevented. However, when the partially stabilized zirconia is kept for

long hours at a temperature between 100 to 300 °C, there is a problem of causing a decrease in mechanical strength of the zirconia. For resolving this problem, a composite ceramic comprising a zirconia matrix and alumina grains dispersed in the zirconia matrix has been proposed. The composite ceramic is capable of improving mechanical properties of the zirconia to some extent, and also preventing the decrease in the mechanical strength of the zirconia when being kept at the temperature between 100 to 300 °C. However, the toughness of the composite ceramic is not sufficiently improved.

In addition, U.S. Patent No. 5,168,080 discloses another composite ceramic having excellent mechanical strength and thermal property. The composite ceramic substantially consists of a first ceramic as a matrix and a second ceramic dispersed in the first ceramic, which has lower sintering temperature and thermal conductivity than the first ceramic. This art also provides a method of manufacturing the composite ceramic. For example, a composite ceramic consisting of silicon nitride as the first ceramic and a partially stabilized zirconia as the second ceramic is manufactured by mixing a silicon powder with a partially stabilized zirconia powder to prepare a mixture powder, pressing the mixture powder to form a green compact with a desired shape, performing a first sintering to the green compact at a first temperature in a nitrogen gas atmosphere to convert silicon to silicon nitride, thereby obtaining a preliminary sintered product, and then performing a second sintering to the

preliminary sintered body at a second temperature higher than the first temperature.

On the other hand, U.S. Patent No. 5,130,210 discloses a solid electrolytic zirconia material comprising a fully stabilized zirconia and a metal oxide such as Al_2O_3 , chromia, mullite or a rare earth metal oxide, etc. The metal oxide is dispersed within grains or in grain boundaries of the stabilized zirconia. By addition of an amount of the stabilizer greater than the amount necessary for obtaining the partially stabilized zirconia, a cubic zirconia phase is stabilized. The zirconia material is capable of improving the mechanical strength thereof without lowering a high ion conductivity of the fully stabilized zirconia. However, since the cubic zirconia phase is not transformed under the stress concentration, the progress of crack in the zirconia is not prevented by the stress induced phase transformation.

Further, U.S. Patent Application No. 769,398 in patent pending discloses a ceramic based composite material comprising a partially stabilized zirconia containing 5 to 30 mol% of CeO_2 as a ceramic matrix and a metal phase of at least one metal element selected from groups IVa, Va and VIa of the periodic table, which is dispersed within grains of the ceramic matrix. The composite material is capable of improving mechanical strength and toughness of the ceramic matrix. However, there is a limitation with respect to a method of manufacturing the composite material. For example, in case of sintering a mixture of the partially stabilized

zirconia and the metal element in a graphite mold or in an usual resistance furnace with a carbon heater, CeO_2 contained as the stabilizer in the partially stabilized zirconia is readily reduced to Ce_2O_3 . Since Ce_2O_3 does not function as the stabilizer, the composite material substantially consists of the metal phase and the monoclinic zirconia phase. Therefore, the toughness of the composite material would not be improved by the stress induced phase transformation. For resolving the above problem, for example, an expensive mold made of alumina or silicon carbide, or an expensive resistance furnace with a molybdenum or tungsten heater has to be used. In addition, when 30 vol% or more of the metal phase, in particular, molybdenum, is contained in the composite material, there is a problem of causing a considerable decrease in the mechanical strength of the composite material.

The present invention is directed to a zirconia based composite material with excellent mechanical strength and toughness, and also a method of manufacturing the same product. That is, the zirconia based composite material comprises a partially stabilized zirconia including 1.5 to 4.5 mol% of yttrium oxide (Y_2O_3) as a matrix and a metal phase of at least one selected from the group consisting of titanium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten. The metal phase has a melting point higher than a sintering temperature of the partially stabilized zirconia, and is dispersed within grains as well as in grain boundaries

of the zirconia matrix. The composite material is manufactured by preparing a mixture of at least one first constituent forming the partially stabilized zirconia and at least one second constituent forming the metal phase, and
5 sintering the mixture in a non-oxidation atmosphere.

Therefore, it is a primary object of the present invention to provide a zirconia based composite material with excellent mechanical strength and toughness and also a method of manufacturing the same product.

10 In a preferred embodiment of the present invention, the composite material further includes a ceramic phase of at least one selected from the group consisting of Al_2O_3 , SiC, Si_3N_4 , B_4C , carbides, nitrides and borides of titanium, vanadium, niobium, tantalum, chromium, molybdenum and
15 tungsten. The composite material contains 0.5 to 50 vol%, and more preferably 20 to 50 vol%, of the metal phase. The content of the metal phase is equal to or less than the content of the partially stabilized zirconia in the composite material. A content of the ceramic phase is equal to or less
20 than the content of the metal phase. The metal phase and ceramic phase are contained in amounts which total 60 vol% of the composite material or less.

In another preferred embodiment of the present invention, the composite material is manufactured by preparing a mixture
25 of at least one first constituent forming the partially stabilized zirconia, at least one second constituent forming the metal phase and at least one third constituent forming the

ceramic phase, and sintering the mixture in the non-oxidation atmosphere.

The zirconia based composite material and the method of manufacturing the same product of the present invention will
5 be detailed hereinafter.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a scanning electron micrograph of a polished surface of the zirconia based composite material of EXAMPLE 9 of the present invention;

10 FIG. 2 is a scanning electron micrograph of the zirconia based composite material of EXAMPLE 9 after thermal etching of a polished surface thereof; and

FIG. 3 is a transmission electron micrograph of the zirconia based composite material of EXAMPLE 9 of the present
15 invention.

DETAIL DESCRIPTION OF THE INVENTION

A zirconia based composite material of the present invention includes a partially stabilized zirconia as a matrix thereof and a metal phase as metal grains dispersed in the
20 zirconia matrix. The partially stabilized zirconia substantially consists of a small amount of a stable monoclinic zirconia phase, or a stable cubic zirconia phase and the balance of a metastable tetragonal zirconia phase. The partially stabilized zirconia contains 1.5 to 4.5 mol% of
25 yttrium oxide (Y_2O_3) as a stabilizer for stabilizing the tetragonal zirconia phase. As the content of Y_2O_3 is smaller, a ratio of the monoclinic zirconia phase relative to the

tetragonal zirconia increases. On the other hand, as the content of Y_2O_3 is greater, a ratio of the cubic zirconia phase relative to the tetragonal zirconia phase increases. The partially stabilized zirconia is known to show the unique phase transformation mechanism capable of improving mechanical strength and toughness thereof, which is generally called as a stress induced phase transformation. When the content of Y_2O_3 is less than 1.5 mol% or more than 4.5 mol%, a ratio of the tetragonal zirconia phase in the zirconia matrix is not enough for improving toughness of the zirconia matrix by the stress induced phase transformation. For effectively improving the toughness of the zirconia matrix, it is further preferred that the content of Y_2O_3 is in the range of 1.6 to 3.2 mol%, and an average grain size of the zirconia matrix is 1.5 μm or less. Additionally, it is not concerned that a combination of Y_2O_3 and at least one selected from the group consisting of magnesium oxide (MgO), calcium oxide (CaO), and cerium oxide (CeO_2), etc., is used as the stabilizer.

The metal phase is at least one selected from the group consisting of titanium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten, each of which has a melting point higher than a sintering temperature of the partially stabilized zirconia. It is preferred that the metal phase having an average grain size of 2 μm or less is dispersed as the metal grains within grains as well as in grain boundaries of the zirconia matrix.

It is preferred that the composite material of the

present invention further includes a ceramic phase of at least one selected from the group consisting of Al_2O_3 , SiC , Si_3N_4 , B_4C , carbides, nitrides and borides of titanium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten, each of which has a higher hardness than the partially stabilized zirconia. It is also preferred that the ceramic phase having an average grain size of $2\text{ }\mu\text{m}$ or less is dispersed as ceramic grains within the grains as well as in the grain boundaries of the zirconia matrix. In case of the composite material including the metal and the ceramic grains, there is a possibility that some of the ceramic grains are dispersed within grains of the metal phase.

The composite material contains 0.5 to 50 vol%, and more preferably 20 to 50 vol%, of the metal phase. The content of the metal phase is equal to or less than the content of the zirconia matrix in the composite material. In case of less than 0.5 vol% of the metal phase, the mechanical strength and toughness of the composite material is not improved sufficiently. In case of 0.5 vol% or more of the metal phase, the metal grains are dispersed within the grains as well as in the grain boundaries of the zirconia matrix. As the content of the metal phase is greater than 20 vol%, local connections formed between adjacent metal grains are observed in the composite material. In addition, in case of more than 40 vol% of the metal phase, elongate successions of the metal phase, in each of which a plurality of metal grains are arranged and connected between adjacent metal grains, as shown in FIG. 2,

are dispersed in the grain boundaries of the zirconia matrix. In this time, there is a possibility that some grains of the zirconia matrix are dispersed within the metal grains.

A toughness improving mechanism of the composite material of the present invention is explained hereinafter. When a crack is generated in the composite material and strikes on one of the metal grains dispersed therein, the crack would take a roundabout way against the metal grain. In general, it is estimated that fracture energy necessary for bowing or deflecting the crack is about 0.5 to 6 J/m². On the other hand, when the crack strikes on one of the elongate successions of the metal phase, there is a probability that the crack cuts through the succession. In this case, since a large amount of energy of the crack is expended in a plastic deformation of the metal phase, a progress of the crack is effectively prevented. As a result, the toughness of the composite material is remarkably improved. It is estimated that the fracture energy necessary for the plastic deformation of the metal phase is about 2000 to 3000 J/m². It is preferred that an aspect ratio of the elongate succession is more than 3 from the viewpoint of the improvement of toughness. By the way, there is a possibility that the successions function as a fracture origin of the composite material, so that the mechanical strength of the composite material is decreased. However, when each of the metal grains included in the successions is 2 μ m or less, the decrease in the strength can be kept to a minimum.

In addition, a residual stress field is formed around each of the metal or ceramic grains in the zirconia matrix due to a mismatch between thermal expansion coefficients of zirconia and the metal phase or the ceramic phase, so that a large number of dislocations are generated within the grains of the zirconia matrix. These dislocations are piled up each other to form sub-grain boundaries in each grain of the zirconia matrix. The formation of such sub-grain boundaries provides a fine grain structure of the zirconia matrix, and also a high critical stress necessary for causing the stress induced phase transformation. Therefore, further improvement of the mechanical strength and toughness of the composite material is achieved by introducing the residual stress field into the zirconia matrix. In particular, when the metal and ceramic grains having the grain size less than $0.1 \mu\text{m}$ are dispersed within the grain as well as in the grain boundaries of the zirconia matrix, the residual stress fields are formed densely and uniformly in the zirconia matrix.

A content of the ceramic phase in the composite material is equal to or less than the content of the metal phase. A sum of the contents of the metal phase and ceramic phase is 60 vol% or less of the composite material. The metal and ceramic grains are capable of inhibiting an undesirable grain growth of the zirconia matrix during sintering, so that a fine grain structure of the zirconia matrix is formed, a size of the fracture origin is decreased, and also the tetragonal zirconia phase is efficiently stabilized. By the way, in case of the

composite material including the ceramic grains dispersed only in the grain boundaries of the zirconia matrix, a hardness of the composite material is increased in proportion to the content of the ceramic phase, based upon a rule of mixtures with respect to hardness. However, when the ceramic grains are dispersed within the grains as well as in the grain boundaries of the zirconia matrix, the hardness of the composite material is more than the hardness given by the rule of mixtures because the dislocations are pinned by the ceramic grains dispersed within the grains of the zirconia matrix.

Methods of manufacturing the zirconia based composite material of the present invention are explained hereinafter. That is, the first method of the present invention comprises the steps of mixing a partially stabilized zirconia powder (hereinafter referred to as "PSZ powder") including 1.5 to 4.5 mol% of Y_2O_3 with a metal powder having an average particle size of $1\mu m$ or less to prepare a first mixture powder, and then sintering the mixture powder in a non-oxidation atmosphere at a sintering temperature lower than the melting point of the metal powder.

The PSZ powder used in the present invention is obtained by, for example, mixing a ZrO_2 powder and a Y_2O_3 powder, or coprecipitating from an aqueous solution of $YCl_3 \cdot 6H_2O$ and $ZrOCl_2 \cdot 8H_2O$. It is preferred that an average particle size of the PSZ powder is $0.5\mu m$ or less for forming a fine grain structure of the zirconia matrix and efficiently stabilizing the tetragonal zirconia phase. When the PSZ powder having an

average particle size more than $0.5\ \mu\text{m}$ is used, there are problems of raising the sintering temperature, causing the undesirable grain growth of the zirconia matrix, and lowering the stability of the tetragonal zirconia phase.

5 The metal powder includes at least one metal element selected from the group consisting of titanium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten. It is preferred that an average particle size of the metal powder is $1\ \mu\text{m}$ or less for decreasing the size of the fracture origin in
10 the composite material. It is further preferred that the average particle size of the metal powder is $0.2\ \mu\text{m}$ or less for dispersing the metal grains within the grains as well as in the grain boundaries of the zirconia matrix. An additive amount of the metal powder is determined in such an amount
15 that the composite material contains 0.5 to 50 vol% of the metal phase, and the content of the metal phase is equal to or less than the content of the zirconia matrix.

It is preferred that the first mixture powder further includes a ceramic powder of at least one ceramic selected
20 from the group consisting of Al_2O_3 , SiC , Si_3N_4 , B_4C , carbides, nitrides and borides of titanium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten, each of which has a higher hardness than the zirconia matrix. It is also preferred that an average grain size of the ceramic powder is less than $1\ \mu\text{m}$,
25 and more preferably $0.2\ \mu\text{m}$ or less, for decreasing the size of the fracture origin of the composite material. An additive amount of the ceramic powder is determined in such an amount

that the content of the ceramic phase is equal to or less than the content of the metal phase, and a sum of the contents of the metal phase and ceramic phase is 60 vol% or less of the composite material.

5 The mixing step of the first method is explained below. That is, the first mixture powder is prepared by utilizing a mixing means like a ball mill, planetary ball mill, or a high energy ball mill which is known as the "Attoritor" available from Union Process Corp., etc., under a wet condition in a
10 solvent such as ethanol, acetone or toluene, or under a dry condition in an inert gas atmosphere such as nitrogen or argon. In case of utilizing the mixing means under the dry condition, it is preferred that an amount of the mixture powder relative to 100 parts by weight of balls of the mixing
15 means is in the range of 1 to 5 parts by weight for achieving a mechanochemical milling. When the metal powder having the average particle size of 1 μ m or more is used in the first method, it is preferred that the first mixture powder is prepared by utilizing the mixing means under the dry
20 condition.

 In addition, it is also preferred that the first mixture powder is prepared by coating the PSZ powder or a granular PSZ powder with the metal element by a PVD (Physical Vapor Deposition) method, incorporating thus coated PSZ powder with
25 the ceramic powder if necessary, and then milling or mixing a resultant by utilizing the mixing means under the wet or dry condition.

The first mixture powder is molded to obtain a green compact with a desired shape by a molding means such as a dry press molding, cold isostatic press (CIP) molding or an injection molding, etc. Subsequently, the green compact is
5 sintered in the non-oxidation atmosphere such as vacuum, the inert gas atmosphere, e.g., nitrogen and argon, or a reducing gas atmosphere, e.g., hydrogen, by utilizing a sintering means such as an atmospheric pressure sintering, vacuum sintering, gas pressure sintering, hot press sintering, or a hot
10 isostatic pressing (HIP) sintering, etc. The non-oxidation atmosphere is adequate for preventing oxidation of the metal powder and non-oxide ceramic powder. The HIP sintering usually comprises the steps of sealing the green compact into a metal or glass capsule, and then keeping the capsule under a
15 hot isostatic pressure. However, it is not concerned that the HIP sintering is utilized for eliminating residual pores in a preliminary sintered product which is formed by the atmospheric pressure sintering, or the hot press sintering, etc., of the green compact.

20 The second method of manufacturing the composite material of the present invention comprises the step of mixing the PSZ powder with a hydride or an oxide of the metal element to prepare a second mixture powder, and then sintering the mixture powder in the reducing gas atmosphere. It is
25 preferred that the second mixture powder is prepared by utilizing the mixing means under the wet or dry condition, as explained in the first method. In particular, when the second

mixture powder is prepared by the mixing means under the dry condition, extremely fine metal grains are dispersed uniformly in the zirconia matrix after the sintering. It is preferred that the second mixture powder further includes the ceramic powder for improving the hardness and mechanical strength of the composite material.

The third method of manufacturing the zirconia based composite material of the present invention comprises the steps of mixing the PSZ powder and an aqueous solution of a salt of the metal element, adding an alkali aqueous solution to thus obtained mixture solution, thereby generating a precipitate, drying and heating the precipitate in an oxidation atmosphere to obtain a third mixture powder which is a crystallized oxide powder of the precipitation, and then sintering the mixture powder in the reducing gas atmosphere. As the alkali aqueous solution, for example, an ammonia aqueous solution or an aqueous solution of potassium hydroxide, etc., is used. Since the precipitate includes an amorphous hydrate of the metal element, the amorphous hydrate is converted to a crystallized metal oxide by the heating step. Therefore, the third mixture powder substantially consists of a powder of the crystallized metal oxide and the PSZ powder. The metal oxide in the third mixture powder is converted again to its metal element during the sintering step in the reducing gas atmosphere, so that extremely fine metal grains are dispersed uniformly in the zirconia matrix. It is also preferred that the mixture solution of the third method

further includes an aqueous solution of an aluminum salt for dispersing fine Al_2O_3 grains in the zirconia matrix.

The forth method of manufacturing the composite material of the present invention comprises the steps of preparing a mixture solution of an aqueous solution of a zirconium salt, an aqueous solution of a yttrium salt and the aqueous solution of the salt of the metal element, adding the alkali aqueous solution to the mixture solution to generate a precipitate, drying and heating the precipitate in the oxidation atmosphere to obtain a fourth mixture powder which is a crystallized oxide powder of the precipitate, and then sintering the mixture powder in the reducing gas atmosphere. A ratio of the aqueous solution of the yttrium salt relative to the aqueous solution of the zirconium salt is determined in such an amount that Y_2O_3 is contained in an amount of 1.5 to 4.5 mol% relative to ZrO_2 to form the partially stabilized zirconia. Since the precipitate of the forth method is amorphous hydrates of yttrium, zirconium and the metal element, the amorphous hydrates are converted to crystallized oxides including an oxide of the metal element and the partially stabilized zirconia by the heating step. Therefore, the forth mixture powder substantially consists of the crystallized oxides. In the forth method, the heating step also has another purpose of forming a solid solution of Y_2O_3 and ZrO_2 to obtain the partially stabilized zirconia. Though the oxide of the metal element is converted to the metal element during the sintering step in the reducing gas atmosphere, the partially stabilized

zirconia is not reduced during the sintering step. It is preferred that the mixture solution of the forth method includes the aqueous solution of the aluminum salt for dispersing fine Al_2O_3 grains in the zirconia matrix.

5 The fifth method of manufacturing the composite material of the present invention comprises the steps of incorporating an organic solution of an alkoxide of the metal element with the aqueous solution of the zirconium salt and the aqueous solution of the yttrium salt, thereby hydrolyzing the
10 alkoxide, adding the alkali aqueous solution to thus obtained mixture solution to generate a precipitate, drying and heating the precipitate in the oxidation atmosphere to obtain a fifth mixture powder which is a crystallized powder of the precipitate, and then sintering the mixture powder in the
15 reducing gas atmosphere. The ratio of the aqueous solution of the yttrium salt relative to the aqueous solution of the zirconium salt is identical to that determined in the forth method. In the mixture solution of the fifth method, the metal alkoxide is hydrolyzed by the aqueous solutions of the
20 yttrium and zirconium salts. Since the precipitate of the fifth method is amorphous hydrates of yttrium, zirconium and the metal element, the amorphous hydrates are converted to crystallized oxides including an oxide of the metal element and the partially stabilized zirconia by the heating step.
25 Therefore, the fifth mixture powder substantially consists of the crystallized oxides. It is preferred that the mixture solution of the fifth method further includes an organic

solution of an aluminum alkoxide or the aqueous solution of the aluminum salt for dispersing the fine Al_2O_3 grains in the zirconia matrix.

5 The sixth method of manufacturing the composite material of the present invention comprises the steps of mixing the PSZ powder with the organic solution of the alkoxide of the metal element, hydrolyzing thus obtained mixture solution to generate a precipitate, drying and heating the precipitate in the oxidation atmosphere to obtain a sixth powder which is a
10 crystallized oxide powder of the precipitate, and then sintering the mixture powder in the reducing gas atmosphere. The mixture solution of the sixth method is hydrolyzed by addition of water thereto. Since the precipitate of the sixth method includes an amorphous hydrate of the metal element, the
15 amorphous hydrate is converted to a crystallized metal oxide by the heating step. Therefore, the sixth mixture powder substantially consists of a powder of the crystallized metal oxide and the PSZ powder. It is preferred that the mixture solution of the sixth method further includes the organic
20 solution of the aluminum alkoxide for dispersing the fine Al_2O_3 grains in the zirconia matrix.

The seventh method of manufacturing the composite material of the present invention comprises the steps of preparing a mixture solution of an organic solution of a
25 zirconium alkoxide, an organic solution of a yttrium alkoxide and the organic solution of the alkoxide of the metal element, hydrolyzing the mixture solution to generate a precipitate,

drying and heating the precipitate in the oxidation atmosphere to obtain a seventh mixture powder which is a crystallized oxide powder of the precipitate, and then sintering the mixture powder in the reducing gas atmosphere. A ratio of the organic solution of the yttrium alkoxide relative to the organic aqueous solution of the zirconium alkoxide is determined in such an amount that Y_2O_3 is contained in an amount of 1.5 to 4.5 mol% relative to ZrO_2 to form the partially stabilized zirconia. Since the precipitate of the seventh method is amorphous hydrates of yttrium, zirconium and the metal element, the amorphous hydrates are converted to crystallized oxides including an oxide of the metal element and the partially stabilized zirconia by the heating step. Therefore, the seventh mixture powder substantially consists of the crystallized oxides. It is preferred that the mixture solution of the seventh method further includes the organic solution of the aluminum alkoxide for dispersing the fine Al_2O_3 grains in the zirconia matrix.

By the way, with respect to any one of the third to seventh methods, it is preferred that the heating step is performed in the air at about 800 °C. It is also preferred that the mixture powder further includes the ceramic powder for improving the hardness and mechanical strength of the composite material. An unique operation consisting of oxidation of the metal element to its metal oxide by the heating step and reduction of the metal oxide to the metal element by the sintering step is very effective for improving

an interfacial bonding strength between the zirconia matrix and the metal grains, and for dispersing fine metal grains less than $0.1\ \mu\text{m}$ uniformly in the zirconium matrix.

The eighth method of manufacturing the composite material of the present invention comprises the steps of mixing the PSZ powder with the metal powder or an oxide powder of the metal element to prepare an eighth mixture powder, heating the mixture powder in the oxidation atmosphere to form a complex oxide powder including a complex oxide of the partially stabilized zirconia and the metal element, and then sintering the complex oxide powder in the reducing gas atmosphere. The heating and sintering steps of the eighth method have the substantially same effect as those of any one of the third to seventh methods. In case that the eighth mixture powder substantially consists of the PSZ powder and the metal powder, the eighth mixture powder is the same as the first mixture powder obtained in the first method. It is preferred that the eighth mixture powder is heated at a temperature of about $500\ ^\circ\text{C}$ to $1200\ ^\circ\text{C}$ in the air to obtain the complex oxide powder. When the complex oxide powder is sintered in the reducing gas atmosphere, the complex oxide is decomposed and reduced again to the metal element and the partially stabilized zirconia, so that the fine metal grains less than $0.1\ \mu\text{m}$ can be dispersed uniformly in the zirconia matrix. It is also preferred that the complex oxide powder is milled by utilizing the mixing means under the wet or dry condition prior to the sintering step. It is another preferred that the complex oxide powder

further includes the ceramic powder for improving the hardness and mechanical properties of the composite material.

In the sintering step of any one of the second to eighth methods, the reducing gas atmosphere has to be maintained until the oxide, or the hydride of the metal element is converted to its metal element. After the conversion, it is not concerned that the sintering step is continued in the non-oxidation atmosphere except for the reducing gas atmosphere. Of course, it is not concerned that the mixing means, molding means, or the sintering means explained in the first method can be utilized against all methods of the present invention.

EXAMPLES 1 to 4 and COMPARATIVE EXAMPLES 1 and 2

Each of zirconia based composite materials of EXAMPLES 1 to 4 and COMPARATIVE EXAMPLES 1 and 2 was manufactured by the following method. That is, a partially stabilized zirconia powder including 0.5 to 6 mol% of yttrium oxide (Y_2O_3) relative to zirconia, as listed on TABLE 1, was mixed with a tungsten (W) powder (average particle size: $0.35 \mu m$, the purity $\geq 99.9\%$) in acetone for 24 hours by a wet ball mill process in such an amount that the composite material substantially consists of 40 vol% of tungsten as W grains and 60 vol% of a partially stabilized zirconia as a matrix thereof, and then dried. A polyethylene vessel and steel balls coated with polyethylene were used in the wet ball mill process. Thus obtained mixture powder was put in a graphite mold, heated from a room temperature to $1000^\circ C$ in a mixture gas atmosphere consisting of 20 vol% of hydrogen and 80 vol% of argon, and further

heated from 1000 °C to 1600 °C under 30 MPa in a decompression atmosphere less than 1.33×10^{-2} Pa. Continuously, the mixture powder was kept at 1600 °C for 1 hour under 30 MPa in the decompression atmosphere according to a hot press sintering process to obtain the composite material which is a disk shape having the diameter of 50 mm and the thickness of 4 mm.

A micro structure of the composite material was observed by a scanning electron microscope (SEM) and a transmission electron microscope (TEM). The composite material was machined to specimens having the sizes of 4 x 3 x 35 mm for measuring mechanical properties thereof, that is, 3 point bending strength (σ_b) and fracture toughness (K_{Ic}). The measurements of the bending strength and fracture toughness was performed in accordance with Japanese Industrial Standard (JIS) R-1601 and the SEPB (Single Edge Precracked Beam) method of JIS R-1607, respectively. Results are shown on TABLE 1. Furthermore, according to a X-ray diffraction analysis, crystal phases of the partially stabilized zirconia of each composite material were identified and also each content of the crystal phases was quantified.

The SEM and TEM observations, the measurements of the mechanical properties, and the X-ray diffraction analysis were performed with respect to all EXAMPLES and COMPARATIVE EXAMPLES in this specification.

Every composite material was sintered to a relative density of 99.5 % or more. It was confirmed by the SEM and TEM observations that every composite material contains fine

tungsten (W) grains having the average grain size of less than 0.1 μm which are dispersed within grains of the zirconia matrix. In particular, it was observed that large W grains having the grain size of about 0.8 μm which are formed by grain growth, and elongate successions consisting of a plurality of the W grains are formed in grain boundaries of the zirconia matrix. It was identified by the X-ray analysis that the partially stabilized zirconia of each composite material of EXAMPLES 1 to 4 consists of less than 10 vol% of a monoclinic phase or cubic phase and the balance of a tetragonal phase. From results of the measurements of the mechanical properties, a partially stabilized zirconia stabilized by addition of 1.5 to 4.5 mol% of Y_2O_3 is preferred as the matrix of the composite material for obtaining excellent mechanical properties.

TABLE 1

	Y_2O_3 Content (mol%)	Crystal Phase of Zirconia	σ_{b3} (MPa)	KIC (MPa $\text{m}^{1/2}$)
EXAMPLE 1	1.5	T+M	1230	9.5
EXAMPLE 2	2.0	T+M	1880	10.2
EXAMPLE 3	3.0	T	1800	11.4
EXAMPLE 4	4.5	T+C	1520	11.0
COMPARATIVE EXAMPLE 1	0.5	M	300	8.3
COMPARATIVE EXAMPLE 2	6.0	T+C	500	8.8

Crystal Phase: T: Tetragonal, M: monoclinic C: Cubic
 σ_{b3} : 3-points bending strength, Kic: Fracture toughness.

EXAMPLES 5 to 10 and COMPARATIVE EXAMPLES 3 to 10

Zirconia based composite materials of EXAMPLES 5 to 10 were manufactured by the substantially same method of EXAMPLES 1 to 4 except that the mixture powder is obtained by mixing a partially stabilized zirconia powder (average particle size: 0.3 μm , 3.0 mol% Y_2O_3) with a molybdenum (Mo) powder (average particle size: 0.65 μm , the purity $\geq 99.9\%$) by the wet ball mill process in such an amount that the individual composite materials substantially consist of the amounts of Mo listed on TABLE 2 as Mo grains and the balance of a partially stabilized zirconia as a matrix thereof after sintering.

On the other hand, a zirconia based composite material of COMPARATIVE EXAMPLE 3 was manufactured by sintering the partially stabilized zirconia powder (average particle size: 0.3 μm , 3.0 mol% Y_2O_3) without mixing with the Mo powder.

In addition, zirconia based composite materials of COMPARATIVE EXAMPLES 4 to 9 were manufactured by the following method. That is, a partially stabilized zirconia powder (average particle size: 0.2 μm , 12.0 mol% cerium oxide (CeO_2)) was mixed with a molybdenum powder (average particle size: 0.65 μm , the purity $\geq 99.9\%$) in acetone for 24 hours by a wet ball mill process in such an amount that the individual composite materials substantially consist of the amounts of Mo listed on TABLE 2 as Mo grains and the balance of a partially stabilized zirconia as a matrix thereof after sintering, and then dried. A polyethylene vessel and polyethylene coated steel balls were used in the wet ball mill process. Thus obtained mixture powder was put in a silicon carbide mold, and

then sintered at about 1600 °C for 1 hour under 30 MPa in argon by using a hot press sintering furnace with a tungsten mesh heater to obtain the composite material which is a disk shape having the diameter of 50 mm and the thickness of 4 mm.

5 Every composite material was sintered to the relative density of 99.5 % or more. It was confirmed by the SEM and TEM observations that every composite material contains fine molybdenum (Mo) grains having the average grain size of less than 0.1 μm which are dispersed within grains of the zirconia
10 matrix. In particular, as the Mo content is greater, it was observed that large Mo grains having the grain size of about 0.8 to 1.2 μm which are formed by grain growth, and elongate successions consisting of a plurality of Mo grains are dispersed in grain boundaries of the zirconia matrix. In
15 addition, as shown in FIGS. 1 and 2, the successions and the fine Mo grains dispersed within the grains of the zirconia matrix were observed in the composite material. In case of 40 vol% or more of the Mo content, the fine Mo grains dispersed within the grains of the zirconia matrix and fine zirconia
20 grains dispersed within the successions of the Mo grains were observed, as shown in FIG. 3. On the other hand, from results of the X-ray diffraction analysis, it is identified that the partially stabilized zirconia of every composite material substantially consists of less than 10 vol% of the monoclinic
25 phase and the balance of the tetragonal phase. It was also confirmed by a chemical analysis that the individual composite materials contain the amounts of Mo listed on TABLE 2.

Results of the measurements of mechanical properties of the composite materials are also listed on TABLE 2.

By the way, with respect to zirconia based composite materials of EXAMPLES 5 to 75 and COMPARATIVE EXAMPLES 3 to 10 mentioned in the present specification, Vickers hardness (H_v) and a dispersion ratio (α) which is a ratio of metal grains dispersed within grains of a partially stabilized zirconia relative to the entire metal grains in the composite material were measured. The dispersion ratio (α) was estimated by counting the number of the metal grains observed in TEM photographs of the composite material.

TABLE 2

	Mo Content (vol%)	σ_{b3} (MPa)	K _{IC} (MPa ^m ^{1/2})	H _v (GPa)	Dispersion ratio α (%)
EXAMPLE 5	5	1080	4.3	11.4	30
EXAMPLE 6	10	1320	4.5	11.2	49
EXAMPLE 7	20	1470	5.4	9.6	41
EXAMPLE 8	30	1600	6.7	8.3	67
EXAMPLE 9	40	1800	11.4	7.1	25
EXAMPLE 10	50	1780	17.5	6.1	15
COMPARATIVE EXAMPLE 3	0	830	3.8	12.1	0
COMPARATIVE EXAMPLE 4	0	550	8.0	8.4	0
COMPARATIVE EXAMPLE 5	5	715	8.4	8.1	39
COMPARATIVE EXAMPLE 6	10	870	8.6	7.8	55
COMPARATIVE EXAMPLE 7	20	960	9.4	7.1	47
COMPARATIVE EXAMPLE 8	30	1060	10.5	6.5	72
COMPARATIVE EXAMPLE 9	40	990	14.1	5.9	31
COMPARATIVE EXAMPLE 10	50	870	19.7	5.2	22

σ_{b3} : 3-points bending strength, K_{IC}: Fracture toughness,
H_v: Vickers hardness

Dispersion ratio α : a ratio of metal grains dispersed within grains of a partially stabilized zirconia relative to the entire metal grains in a zirconia based composite material

When the matrix of the composite material is the partially stabilized zirconia stabilized by addition of 12 mol% of CeO₂, the bending strength tends to decrease as the Mo

content is greater than 30 vol%, as shown in COMPARATIVE
EXAMPLES 8 to 10 on TABLE 2. On the other hand, when the
matrix of the composite material is the partially stabilized
zirconia stabilized by addition of 3 mol% of Y_2O_3 , the bending
5 strength is increased in proportion to the Mo content, as
shown in EXAMPLES 8 to 10 on TABLE 2. Therefore, the
composite material in the present invention can contain more
than 30 vol% of Mo for improving the toughness without
decreasing the bending strength thereof.

10

EXAMPLE 11

A zirconia based composite material of EXAMPLE 11 was
manufactured by the substantially same method as EXAMPLES 1 to
4 except that the mixture powder is prepared by mixing a
partially stabilized zirconia powder (average particle size:
15 0.3 μm , 3.0 mol% Y_2O_3) with a molybdenum (Mo) powder (average
grain size: 3 μm , the purity $\geq 99.9\%$) by the wet ball mill
process in such an amount the composite material substantially
consists of 40 vol% of Mo as Mo grains and 60 vol% of a
partially stabilized zirconia as a matrix thereof after
20 sintering..

The composite material of EXAMPLE 11 was sintered to a
relative density more than 99.5 %. The Mo grains are
dispersed only in grain boundaries of the partially stabilized
zirconia matrix. In comparison with the composite material of
25 EXAMPLE 9 in which the Mo powder having the average grain size
of 0.65 μm is used as an original powder, it is known that a
fine Mo powder is preferable as the original powder to

disperse the Mo grains within grains of the zirconia matrix and improve mechanical properties of the composite material.

TABLE 3

	Mo Content (vol%)	σ_{bs} (MPa)	K _{IC} (MPa ^{m^{1/2}})	H _v (GPa)	Dispersion ratio α (%)
5 EXAMPLE 11	40	880	11.0.	6.9	0

EXAMPLES 12 to 16

Zirconia based composite materials of EXAMPLES 12 to 16 were manufactured by the substantially same method as EXAMPLES 1 to 4 except that the mixture powder is prepared by mixing a partially stabilized zirconia powder (average particle size: 0.3 μm , 3 mol% Y_2O_3) with a Mo powder (average particle size: 0.65 μm , the purity ≥ 99.9 %) and a ceramic powder (average particle size: 1 μm or less) by the wet ball mill process in such an amount that the individual composite materials substantially consist of 20 vol% of Mo as Mo grains, 20 vol% of ceramics listed on TABLE 4 as ceramic grains, and 60 vol% of a partially stabilized zirconia as a matrix thereof after sintering. An aluminum oxide powder of EXAMPLE 12 is $\gamma\text{-Al}_2\text{O}_3$. A silicon carbide powder of EXAMPLE 13 is $\beta\text{-SiC}$.

Every composite material was sintered to a relative density of 99.5 % or more. It was confirmed by the SEM and TEM observations that every composite material contains fine Mo grains having the average grain size of less than 0.1 μm and fine ceramic grains having the average grain size of about 0.3 μm , which are dispersed within grains of the zirconia matrix. In particular, it was observed that large Mo grains having the grain size of about 0.8 to 1.2 μm which are formed

by grain growth, large ceramic grains having the almost same grain size as the large Mo grains, and elongate successions consisting of a plurality of Mo grains are dispersed in the grain boundaries of the zirconia matrix. In addition, from results of the X-ray analysis and the chemical analysis, it was confirmed that the partially stabilized zirconia of each composite material consists of 5 vol% or less of the monoclinic phase and the balance of the tetragonal phase, and the individual composite materials accurately contain the amounts of Mo and the ceramics listed on TABLE 4. Results of the measurements of mechanical properties of the composite materials of EXAMPLE 12 to 16 are shown on TABLE 4.

By the way, with respect to zirconia based composite materials of EXAMPLES 12 to 16, and 71 to 75, the dispersion ratio (α) and a dispersion ratio (β), which is a ratio of ceramic grains dispersed within grains of a partially stabilized zirconia relative to the entire ceramic grains in the composite material, were measured. The dispersion ratio (β) was estimated by counting the number of the ceramic grains in TEM photographs of the composite material.

TABLE 4

	Ceramic	σ_{b3} (MPa)	K_{Ic} (MPa $m^{1/2}$)	H_v (GPa)	Dispersion ratio α (%)	Dispersion ratio β (%)
EXAMPLE 12	Al ₂ O ₃	1790	6.2	10.4	15	31
EXAMPLE 13	SiC	1700	6.4	12.0	12	36
EXAMPLE 14	TiC	1650	6.7	12.4	15	27
EXAMPLE 15	B ₄ C	1580	7.1	15.2	14	25
EXAMPLE 16	WC	1740	6.5	10.8	14	29

σ_{bs} : 3-points bending strength, K_{Ic} : Fracture toughness,
Hv: Vickers Hardness

Dispersion ratio α : a ratio of metal grains dispersed within grains of a partially stabilized zirconia relative to the entire metal grains in a zirconia based composite material

Dispersion ratio β : a ratio of ceramic grains dispersed within the grains of the partially stabilized zirconia relative to the entire ceramic grains in the composite material.

EXAMPLES 17 to 33

Zirconia based composite materials of EXAMPLES 17 to 23 were manufactured by the following method. That is, a partially stabilized zirconia (PSZ) powder (average particle size: $0.3 \mu\text{m}$, 3.0 mol% Y_2O_3) was mixed with a metal powder (average particle size: $1 \mu\text{m}$ or more, the purity $\geq 99.9\%$), or two kinds of the metal powder, by a planetary dry ball mill process in argon for 48 hours in such an amount that the individual composite materials substantially consist of the amounts of metal elements listed on TABLE 5 as metal grains and 60 vol% of a partially stabilized zirconia as a matrix thereof after sintering, and then dried. A pot and balls of the planetary ball mill process are made of a partially stabilized zirconia. An amount of thus obtained mixture powder relative to 100 parts by weight of the balls was 1 to 5 parts by weight. The mixture powder was put in a graphite mold, heated from a room temperature to 1000°C in hydrogen, and further heated from 1000°C to 1600°C under 30 MPa in a decompression atmosphere less than 1.33×10^{-2} Pa. Continuously, the mixture powder was sintered at 1600°C for 1 hour under 30 MPa in the decompression atmosphere according to

a hot press sintering process to obtain the composite material which is a disc shape having the diameter of 50 mm and the thickness of 4 mm.

On the other hand, zirconia based composite materials of
5 EXAMPLES 24 to 28 were manufactured by the following method.
That is, a partially stabilized zirconia (PSZ) powder (average
particle size: $0.3\ \mu\text{m}$, 3 mol% Y_2O_3) was coated with a metal
element (the purity: $\geq 99.9\%$) to prepare a composite powder
according to a PVD method in such an amount that the
10 individual composite materials substantially consist of 10
vol% of the metal elements listed on TABLE 6 as metal grains
and 90 vol% of a partially stabilized zirconia as a matrix
thereof after sintering. The composite powder was milled in
acetone for 48 hours by a wet ball mill process, and then
15 dried. A vessel and balls used in the wet ball mill process
is made of Al_2O_3 . Thus obtained mixture powder was put in a
graphite mold, heated from a room temperature to $1000\ ^\circ\text{C}$ in a
mixture gas atmosphere consisting 20 vol% of hydrogen and 80
vol% of argon, and further heated from $1000\ ^\circ\text{C}$ to $1500\ ^\circ\text{C}$
20 under 30 MPa in a decompression atmosphere less than 1.33×10^{-2} Pa.
Continuously, the mixture powder was sintered at $1500\ ^\circ\text{C}$
for 1 hour under 30 MPa in the decompression atmosphere
according to a hot press sintering process to obtain the
composite material which is a disc shape having the diameter
25 of 50 mm and the thickness of 4 mm.

In addition, zirconia based composite materials of
EXAMPLES 29 to 33 were manufactured by the substantially same

method as EXAMPLES 24 to 28 except that the composite powder is prepared by adding polyvinyl alcohol to the PSZ powder (average particle size: $0.3\ \mu\text{m}$, 3 mol% Y_2O_3) to obtain a mixture including 3 wt% of polyvinyl alcohol, forming a granular powder of the mixture having the average grain size of about $50\ \mu\text{m}$ by a spray-dry process, and then coating a metal element (the purity: $\geq 99.9\%$) on the granular powder according to the PVD method in such an manner that the individual composite materials substantially consist of 20 vol% of the metal elements listed on TABLE 7 as metal grains and 80 vol% of the partially stabilized zirconia as a matrix thereof after sintering.

Every composite material was sintered to a relative density of 99.5 % or more. It was confirmed by the SEM and TEM observations that every composite material contains fine metal grains having an average grain size of less than $0.1\ \mu\text{m}$ which are dispersed within grains of the zirconia matrix. In particular, it was observed that large metal grains having the grain size of about $0.8\ \mu\text{m}$ which are formed by grain growth and elongate successions consisting of a plurality of metal grains are dispersed in the grain boundaries of the zirconia matrix. In addition, from results of the X-ray analysis and the chemical analysis, it was confirmed that when the partially stabilized zirconia of each composite material consists of 5 vol% or less of the monoclinic phase or the cubic phase and the balance of the tetragonal phase, and the individual composite materials accurately contain the amounts

of metal elements listed on TABLES 5, 6 and 7. Results of the measurements of mechanical properties of the composite materials of EXAMPLE 17 to 33 are also shown on TABLES 5, 6 and 7.

TABLE 5

	Metal Content	σ_{bs} (MPa)	K_{Ic} (MPam ^{1/2})	Hv (GPa)	Dispersion Ratio α (%)
EXAMPLE 17	40 vol% Ti	1830	12.3	7.5	30
EXAMPLE 18	40 vol% V	1800	10.8	7.2	29
EXAMPLE 19	40 vol% Nb	1820	10.7	7.7	30
EXAMPLE 20	40 vol% Ta	1870	10.6	7.9	31
EXAMPLE 21	40 vol% Cr	1880	11.3	7.6	28
EXAMPLE 22	20 vol% W & 20 vol% Mo	1780	9.3	8.3	32
EXAMPLE 23	20 vol% W & 20 vol% Ti	1800	9.8	8.0	29

TABLE 6

	Metal	σ_{bs} (MPa)	K_{Ic} (MPam ^{1/2})	Hv (GPa)	Dispersion Ratio α (%)
EXAMPLE 24	Ti	1440	6.7	11.4	41
EXAMPLE 25	V	1460	5.6	11.1	41
EXAMPLE 26	Nb	1430	5.4	11.6	40
EXAMPLE 27	Ta	1490	5.1	11.5	43
EXAMPLE 28	Cr	1500	5.8	11.2	39

TABLE 7

	Metal	σ_{b3} (MPa)	K_{Ic} (MPa $m^{1/2}$)	H_v (GPa)	Dispersion ratio α (%)
EXAMPLE 29	Ti	1700	7.6	9.8	35
EXAMPLE 30	V	1720	6.4	9.5	33
EXAMPLE 31	Nb	1690	6.2	10.2	33
EXAMPLE 32	Ta	1740	5.9	10.1	36
EXAMPLE 33	Cr	1750	6.6	9.8	31

σ_{b3} : 3-points bending strength, K_{Ic} : Fracture toughness,
 H_v : Vickers Hardness

Dispersion ratio α : a ratio of metal grains dispersed within grains of a partially
stabilized zirconia relative to the entire metal grains in a
zirconia based composite material

EXAMPLES 34 to 38

Zirconia based composite materials of EXAMPLES 34 and 35 were manufactured by the substantially same method as EXAMPLES 1 to 4 except that the mixture powder is prepared by mixing a partially stabilized powder (PSZ) powder (average particle size: 0.3 μm , 3 mol% of Y_2O_3) with a metal oxide powder (average particle size: about 0.8 μm) by the wet ball mill process in such an amount that the individual composite materials substantially consist of 40 vol% of the metal elements resulting from reducing the metal oxides listed on TABLE 8 as metal grains and 60 vol% of a partially stabilized zirconia as a matrix thereof after sintering, and the mixture powder was heated from the room temperature to 1000 °C in hydrogen.

On the other hand, zirconia based composite materials of EXAMPLES 36 to 38 were manufactured by the substantially same

method as EXAMPLES 17 to 23 except that the mixture powder was prepared by mixing the PSZ powder (average particle size: 0.3 μm , 3 mol% of Y_2O_3) with a metal oxide or a metal hydride powder (average particle size: 1 μm or more, the purity:
5 $\geq 99.9\%$) by the planetary dry ball mill process in the air in such an amount that the individual composite materials substantially consist of 40 vol% of the metal elements resulting from reducing the metal oxides and metal hydride listed on TABLE 9 as metal grains and 60 vol% of the partially
10 stabilized zirconia as a matrix thereof after sintering.

Every composite material was sintered to a relative density of 99.5 % or more. It was confirmed by the SEM and TEM observations that every composite material contains fine metal grains having an average grain size of less than 0.1 μm
15 which are dispersed within grains of the zirconia matrix. In particular, it was observed that large metal grains having the grain size of about 0.8 μm which are formed by grain growth and elongate successions consisting of a plurality of metal grains are dispersed in grain boundaries of the zirconia
20 matrix. When the dispersion ratio α of EXAMPLE 35 is compared with the ratio α of EXAMPLE 9, it is understood that the metal oxide powder is further preferred as an original powder for efficiently dispersing the metal grains within the grains of the zirconia matrix than the metal powder. In addition, from
25 results of the X-ray analysis and chemical analysis, it was confirmed that the partially stabilized zirconia of each composite material consists of 5 vol% or less of the

monoclinic phase and the balance of the tetragonal phase, and each metal oxide listed on TABLES 8 and 9 was completely reduced to its metal element by the sintering. Results of the measurements of mechanical properties of the composite materials of EXAMPLES 34 to 38 are also shown on TABLES 8 and 9.

TABLE 8

	Metal Oxide	σ_b (MPa)	K_{Ic} (MPa $m^{1/2}$)	H_v (GPa)	Dispersion ratio α (%)
EXAMPLE 34	WO ₃	1900	11.7	7.6	36
EXAMPLE 35	MoO ₃	1920	11.9	7.8	36

TABLE 9

	Metal Oxide	σ_b (MPa)	K_{Ic} (MPa $m^{1/2}$)	H_v (GPa)	Dispersion ratio α (%)
EXAMPLE 36	Nb ₂ O ₅	1820	11.3	8.0	38
EXAMPLE 37	V ₂ O ₅	1880	11.6	7.5	38
EXAMPLE 38	TiH ₂	1860	12.1	7.7	39

EXAMPLE 39 and 40

A zirconia based composite material of EXAMPLE 39 was manufactured by the following method. That is, a partially stabilized zirconia (PSZ) powder (average particle size: 0.3 μ m, 3 mol% of Y₂O₃) was mixed with a WO₃ powder (average particle size: 0.8 μ m, the purity: \geq 99.9%) by a wet ball mill process in acetone for 72 hours in such an amount that the composite material substantially consists of 40 vol% of tungsten resulting from reducing WO₃ as metal grains and 60 vol% of a partially stabilized zirconia as a matrix thereof after sintering, and then dried to prepare a mixture powder.

The mixture powder was heated at about 1150 °C for 12 hours in the air to form a complex oxide powder including the partially stabilized zirconia and ZrW_2O_8 . The complex oxide powder was milled by a dry ball mill process in the air for 24 hours.

5 Thus milled complex oxide powder was put in a graphite mold, heated from a room temperature to 1000 °C in hydrogen, and further heated from 1000 °C to 1600 °C under 30 MPa in a decompression atmosphere less than 1.33×10^{-2} Pa. Continuously, the complex oxide powder was sintered at 1600 °C
10 for 1 hour under 30 MPa in the decompression atmosphere according to a hot press sintering process to obtain the composite material which is a disc shape having the diameter of 50 mm and the thickness of 4 mm.

On the other hand, a zirconia based composite material of
15 EXAMPLE 40 was manufactured by the substantially same method as EXAMPLE 34 except that the mixture powder was prepared by mixing the PSZ powder with a MoO_3 powder (average particle size: 0.8 μm , the purity: $\geq 99.9\%$) by the wet ball mill process in such an amount that the composite material substantially
20 consists of 40 vol% of molybdenum resulting from reducing MoO_3 as metal grains and 60 vol% of the partially stabilized zirconia as a matrix thereof after sintering, and the mixture powder was heated at about 700 °C for 12 hours in the air to form a complex oxide powder including the partially stabilized
25 zirconia and $\text{Zr}(\text{MoO}_4)_2$.

Both composite material were sintered to a relative density of 99.5 % or more. It was confirmed by the SEM and

TEM observations that each composite material contains fine metal grains having an average grain size of less than $0.1 \mu\text{m}$ which are dispersed within grains of the zirconia matrix. In particular, it was observed that large metal grains having the grain size of about $0.8 \mu\text{m}$ which are formed by grain growth and elongate successions consisting of a plurality of metal grains are dispersed in grain boundaries of the zirconia matrix. In addition, from results of the X-ray diffraction analysis and chemical analysis, it was identified that the partially stabilized zirconia of each composite material of EXAMPLES 39 and 40 consists of 5 vol% or less of the monoclinic phase and the balance of the tetragonal phase, and the complex oxide of every mixture powder was decomposed and reduced to its metal element and the partially stabilized zirconia by the sintering. Results of the measurements of mechanical properties of the composite materials of EXAMPLES 39 and 40 are also shown on TABLE 10.

TABLE 10

	Metal Oxide	σ_{b3} (MPa)	K_{Ic} (MPa $\text{m}^{1/2}$)	H_v (GPa)	Dispersion ratio α (%)
EXAMPLE 39	WO_3	1940	11.5	8.0	39
EXAMPLE 40	MoO_3	1970	11.6	8.2	41

EXAMPLES 41 to 70

Zirconia based composite materials of EXAMPLES 41 to 46 were manufactured by the following method. That is, a partially stabilized zirconia (PSZ) powder (average grain size: $0.3 \mu\text{m}$, 3 mol% Y_2O_3) was mixed with an aqueous solution

of MoCl_5 to prepare a mixture solution in such an amount that the individual composite materials substantially consist of the amounts of Mo listed on TABLE 11 as metal grains and the balance of a partially stabilized zirconia as a matrix thereof after sintering. Subsequently, an ammonia aqueous solution was dropped into the mixture solution until pH of the mixture solution became to 8 while agitating the mixture solution, so that a sol precipitation was generated. The sol precipitation was washed with water, dehydrated, dried, and then kept at about 800 °C for 3 hours in the air to obtain a mixture powder of the partially stabilized zirconia and MoO_3 . The mixture powder was put in a graphite mold, heated from a room temperature to 1000 °C in hydrogen, and further heated from 1000 °C to 1600 °C under 30 MPa in a decompression atmosphere less than 1.33×10^{-2} Pa. Continuously, the mixture powder was sintered at 1600 °C for 1 hour under 30 MPa in the decompression atmosphere according to a hot press sintering process to obtain the composite material.

Zirconia based composite materials of EXAMPLE 47 to 52 were manufactured by the substantially same method as EXAMPLES 41 to 46 except that the mixture solution was prepared by mixing a first aqueous solution including $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and YCl_3 with a second aqueous solution of VCl_2 in such an amount that the individual composite materials substantially consist of the amounts of vanadium (V) listed on TABLE 12 as metal grains and the balance of a partially stabilized zirconia as a matrix thereof after sintering, wherein the concentration of YCl_3 of

the first aqueous solution was determined in such an amount that the partially stabilized zirconia contains 3 mol% of Y_2O_3 , and also the mixture powder substantially consists of the partially stabilized zirconia and V_2O_5 .

5 Zirconia based composite materials of EXAMPLE 53 to 58 were manufactured by the substantially same method as EXAMPLES 41 to 46 except that the mixture solution was prepared by mixing a first aqueous solution including $ZrOCl_2 \cdot 8H_2O$ and YCl_3 with an ethanol solution of $W(OC_2H_5)_5$ in such an amount that
10 the individual composite materials substantially consist of the amounts of tungsten (W) listed on TABLE 13 as metal grains and the balance of a partially stabilized zirconia as a matrix thereof after sintering, wherein the concentration of YCl_3 of
15 the first aqueous solution was determined in such an amount that the partially stabilized zirconia contains 3 mol% of Y_2O_3 , and also the mixture powder substantially consists of the partially stabilized zirconia and WO_3 .

 Zirconia based composite materials of EXAMPLES 59 to 64 were manufactured by the following method. That is, a
20 partially stabilized zirconia (PSZ) powder (average grain size: $0.3 \mu m$, 3 mol% Y_2O_3) was mixed with an ethanol solution of $Nb(OC_2H_5)_5$ to obtain a mixture solution in such an amount that the individual composite materials substantially consists
25 of the amounts of niobium (Nb) listed on TABLE 14 as metal grains and the balance of a partially stabilized zirconia as a matrix thereof after sintering. The mixture solution was hydrolyzed by addition of water thereto to generate a

precipitation. The precipitation was dried, and then heated at about 800 °C for 4 hours in the air to obtain a mixture powder substantially consisting of the partially stabilized zirconia and Nb₂O₅. The mixture powder was put in a graphite mold, heated from a room temperature to 1000 °C in hydrogen, and further heated from 1000 °C to 1600 °C under 30 MPa in a decompression atmosphere less than 1.33×10^{-2} Pa. Continuously, the mixture powder was sintered at 1600 °C for 1 hour under 30 MPa in the decompression atmosphere according to a hot press sintering process to obtain the composite material.

Zirconia based composite materials of EXAMPLES 65 to 70 were manufactured by the substantially same method as EXAMPLES 59 to 64 except that the mixture solution was prepared by mixing a first isopropyl alcohol solution of Zr(OC₂H₅)₄ and Y(O-CH(CH₃)₂)₃ with a second isopropyl alcohol solution of Mo(OC₂H₅)₅ in such an amount that the individual composite materials substantially consist of the amounts of molybdenum (Mo) listed on TABLE 15 as metal grains and the balance of a partially stabilized zirconia as a matrix thereof after sintering, wherein the concentration of Y(O-CH(CH₃)₂)₃ in the first isopropyl alcohol solution was determined in such an amount that the partially stabilized zirconia contains 3 mol% of Y₂O₃, and also the mixture powder substantially consists of the partially stabilized zirconia and MoO₃.

Every composite material is a disc shape having the diameter of 50 mm and the thickness of 4 mm, and was sintered

to a relative density of 99.5 % or more. It was confirmed by the SEM and TEM observations that every composite material contains fine metal grains having an average grain size of less than 0.1 μm which are dispersed within grains of the zirconia matrix. In particular, as a metal content is greater, it was observed that large metal grains having an grain size of about 0.8 to 1.2 μm which are formed by grain growth and elongate successions consisting of a plurality of metal grains are dispersed in grain boundaries of the zirconia matrix. In composite materials having 40 vol% or more of the metal content, the fine metal grains dispersed within the grains of the zirconia matrix and zirconia grains dispersed within the successions of the metal grains were observed. On the other hand, from results of the X-ray analysis and chemical analysis, it was identified that the partially stabilized zirconia of each composite material consists of 10 vol% or less of the monoclinic phase and the balance of the tetragonal phase, and the metal oxide except for the partially stabilized zirconia of every mixture powder was completely reduced to its metal element by the sintering. Results of measurements of mechanical properties of the composite materials of EXAMPLES 41 to 70 are also shown on TABLES 11 to 15.

TABLE 11

	Mo Content (vol%)	σ_{b3} (MPa)	K_{Ic} (MPa $m^{1/2}$)	H_v (GPa)	Dispersion ratio α (%)
EXAMPLE 41	5	1300	3.9	12.0	36
EXAMPLE 42	10	1490	4.2	11.7	53
EXAMPLE 43	20	1720	4.9	10.1	43
EXAMPLE 44	30	1790	5.6	9.2	69
EXAMPLE 45	40	1880	10.2	7.8	41
EXAMPLE 46	50	1900	16.1	7.0	27

TABLE 12

	V Content (vol%)	σ_{b3} (MPa)	K_{Ic} (MPa $m^{1/2}$)	H_v (GPa)	Dispersion ratio α (%)
EXAMPLE 47	5	1230	3.6	11.5	37
EXAMPLE 48	10	1420	4.0	10.2	53
EXAMPLE 49	20	1670	4.5	9.5	45
EXAMPLE 50	30	1740	5.3	8.6	69
EXAMPLE 51	40	1830	9.8	7.6	43
EXAMPLE 52	50	1890	15.5	6.5	26

TABLE 13

	W Content (vol%)	σ_{b3} (MPa)	K_{Ic} (MPa $m^{1/2}$)	H_v (GPa)	Dispersion ratio α (%)
EXAMPLE 53	5	1280	3.8	11.8	36
EXAMPLE 54	10	1470	4.0	11.4	55
EXAMPLE 55	20	1690	4.8	10.6	46
EXAMPLE 56	30	1760	5.5	9.8	67
EXAMPLE 57	40	1880	10.1	9.1	40
EXAMPLE 58	50	1920	16.4	8.4	24

TABLE 14

	Nb Content (vol%)	σ_{b3} (MPa)	K _{IC} (MPa ^{1/2})	H _v (GPa)	Dispersion ratio α (%)
EXAMPLE 59	5	1240	3.4	11.7	34
EXAMPLE 60	10	1430	3.9	11.2	52
EXAMPLE 61	20	1650	4.3	10.1	41
EXAMPLE 62	30	1700	5.1	9.0	62
EXAMPLE 63	40	1860	9.7	7.9	37
EXAMPLE 64	50	1980	16.0	6.8	21

TABLE 15

	Mo Content (vol%)	σ_{b3} (MPa)	K _{IC} (MPa ^{1/2})	H _v (GPa)	Dispersion ratio α (%)
EXAMPLE 65	5	1300	3.9	12.0	38
EXAMPLE 66	10	1500	4.1	11.7	54
EXAMPLE 67	20	1750	4.8	10.3	43
EXAMPLE 68	30	1800	5.5	9.4	69
EXAMPLE 69	40	1890	10.1	7.9	44
EXAMPLE 70	50	1900	16.0	7.1	30

σ_{b3} : 3-points bending strength, K_{IC}: Fracture toughness,
H_v: Vickers Hardness

Dispersion ratio α : a ratio of metal grains dispersed within grains of a partially
stabilized zirconia relative to the entire metal grains in a
zirconia based composite material

EXAMPLES 71 to 75

A zirconia based composite material of EXAMPLE 71 was
manufactured by the substantially same method as EXAMPLES 41
to 46 except that the mixture solution was prepared by mixing
the PSZ powder (average grain size: 0.3 μ m, 3 mol% Y₂O₃) with
an aqueous solution including MoCl₅ and Al(NO₃)₃·9H₂O in such an
amount that the composite material substantially consists of
40 vol% of the partially stabilized zirconia as a matrix

thereof, 40 vol% of Mo as metal grains and 20 vol% of Al_2O_3 as ceramic grains after sintering, and also the mixture powder substantially consists of the partially stabilized zirconia, MoO_3 and Al_2O_3 .

5 A zirconia based composite material of EXAMPLE 72 was manufactured by the substantially same method as EXAMPLES 41 to 46 except that the mixture solution was prepared by mixing a first aqueous solution including $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and YCl_3 with a second aqueous solution of VCl_2 and a third aqueous solution of
10 $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ in such an amount that the composite material substantially consists of 40 vol% of the partially stabilized zirconia as a matrix thereof, 40 vol% of vanadium as metal grains and 20 vol% of Al_2O_3 as ceramic grains after sintering, wherein the concentration of YCl_3 of the first aqueous solution
15 was determined in such an amount that the partially stabilized zirconia contains 3 mol% of Y_2O_3 , and also the mixture powder substantially consists of the partially stabilized zirconia, V_2O_5 and Al_2O_3 .

 A zirconia based composite material of EXAMPLES 73 was
20 manufactured by the substantially same method as EXAMPLES 41 to 46 except that the mixture solution was prepared by mixing a first aqueous solution including $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and YCl_3 with a first ethanol solution of $\text{W}(\text{OC}_2\text{H}_5)_6$ and a second ethanol solution of $\text{Al}(\text{O}-\text{CH}(\text{CH}_3)_2)_3$ in such an amount that the
25 composite material substantially consists of 40 vol% of the partially stabilized zirconia as a matrix thereof, 40 vol% of tungsten as metal grains and 20 vol% of Al_2O_3 as ceramic grains

after sintering, wherein the concentration of YCl_3 of the first aqueous solution was determined in such an amount that the partially stabilized zirconia contains 3 mol% of Y_2O_3 , and also the mixture powder substantially consists of the partially stabilized zirconia, WO_3 and Al_2O_3 .

A zirconia based composite material of EXAMPLES 74 was manufactured by the substantially same method as EXAMPLES 59 to 64 except that the mixture powder was prepared by mixing the PSZ powder (average grain size: $0.3 \mu m$, 3 mol% Y_2O_3) with the ethanol solution of $Nb(OC_2H_5)_5$ and a second ethanol solution of $Al(O-CH(CH_3)_2)_3$ in such an amount that the composite material substantially consists of 40 vol% of the partially stabilized zirconia as a matrix thereof, 40 vol% of niobium as metal grains and 20 vol% of Al_2O_3 as ceramic grains after sintering, and also the mixture powder substantially consists of the partially stabilized zirconia, Nb_2O_5 and Al_2O_3 .

A zirconia based composite material of EXAMPLES 75 was manufactured by the substantially same method as EXAMPLES 59 to 64 except that the mixture solution was prepared by mixing a first isopropyl alcohol solution of $Zr(OC_2H_5)_4$ and $Y(O-CH(CH_3)_2)_3$ with a second isopropyl alcohol solution of $Mo(OC_2H_5)_5$ and a third isopropyl alcohol solution of $Al(O-CH(CH_3)_2)_3$ in such an amount that the composite material substantially consists of 40 vol% of the partially stabilized zirconia as a matrix thereof, 40 vol% of Mo as metal grains and 20 vol% of Al_2O_3 as ceramic grains after sintering, wherein the concentration of $Y(O-CH(CH_3)_2)_3$ in the first isopropyl alcohol

solution was determined in such an amount that the partially stabilized zirconia contains 3 mol% of Y_2O_3 , and also the mixture powder substantially consists of the partially stabilized zirconia, Nb_2O_5 and Al_2O_3 .

5 Every composite material is a disc shape having the diameter of 50 mm and the thickness of 4 mm, and was sintered to a relative density of 99.5 % or more. It was confirmed by the SEM and TEM observations that every composite material contains fine metal and Al_2O_3 grains having an average grain
10 size of less than $0.1 \mu m$ which are dispersed within grains of the zirconia matrix. In particular, it was observed that large metal grains having a grain size of about 0.8 to $1.2 \mu m$ which are formed by grain growth and elongate successions consisting of a plurality of metal grains are dispersed in
15 grain boundaries of the zirconia matrix. In addition, it was confirmed that the fine Al_2O_3 grains are dispersed within the successions of the metal grains. On the other hand, from results of the X-ray analysis and chemical analysis, it was identified that the partially stabilized zirconia of every
20 composite material consists of 5 vol% or less of the monoclinic phase and the balance of the tetragonal phase, and the metal oxide except for the partially stabilized zirconia and Al_2O_3 of every mixture powder was completely reduced to its metal element by the sintering. Results of measurements of
25 mechanical properties of the composite materials of EXAMPLES 71 to 75 are also shown on TABLE 16.

TABLE 16

	Content (vol%)		σ_{b3} (MPa)	K_{Ic} (MPam ^{1/2})	H_v (GPa)	Dispersion ratio α (%)	Dispersion ratio β (%)
	Metal	Al ₂ O ₃					
EXAMPLE 71	Mo, 40	20	1770	14.8	9.8	14	12
EXAMPLE 72	V, 40	20	1740	13.7	9.2	16	14
EXAMPLE 73	W, 40	20	1760	14.0	10.7	18	17
EXAMPLE 74	Nb, 40	20	1710	13.7	9.4	15	12
EXAMPLE 75	Mo, 40	20	1820	14.3	9.7	19	18

σ_{b3} : 3-points bending strength, K_{Ic} : Fracture toughness,
 H_v : Vickers Hardness

Dispersion ratio α : a ratio of metal grains dispersed within grains of a partially
 stabilized zirconia relative to the entire metal grains in a
 zirconia based composite material

Dispersion ratio β : a ratio of ceramic grains dispersed within grains of the
 partially stabilized zirconia relative to the entire ceramic
 grains in the composite material

CLAIMS

1. A zirconia based composite material comprising a partially
stabilized zirconia including 1.5 to 4.5 mol% of yttrium oxide
5 and a metal phase of at least one selected from the group
consisting of titanium, vanadium, niobium, tantalum, chromium,
molybdenum and tungsten, said metal phase having a melting
point higher than a sintering temperature of said partially
stabilized zirconia.

10

2. A zirconia based composite material as set forth in claim
1, wherein said metal phase is dispersed within grains as well
15 as in grain boundaries of said partially stabilized zirconia.

3. A zirconia based composite material as set forth in claim 1
20 or 2, wherein said composite material includes said partially
stabilized zirconia dispersed within grains of said metal
phase.

25

4. A zirconia based composite material as set forth in claim
1, wherein said composite material contains 0.5 to 50 vol% of

said metal phase.

- 5 5. A zirconia based composite material as set forth in claim 2, wherein said composite material contains 20 to 50 vol% of said metal phase.

10

6. A zirconia based composite material as set forth in claim 1, wherein an average grain size of said partially stabilized zirconia is 1.5 μm or less, and an average grain size of said metal phase is 2 μm or less.

15

7. A zirconia based composite material as set forth in claim 1, wherein said composite material further includes a ceramic phase of at least one selected from the group consisting of Al_2O_3 , SiC , Si_3N_4 , B_4C , carbides, nitrides and borides of titanium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten.

25

8. A zirconia based composite material as set forth in claim

7, wherein said ceramic phase is dispersed within grains as well as in grain boundaries of said partially stabilized zirconia.

5

9. A zirconia based composite material as set forth in claim 7, wherein said composite material includes said ceramic phase dispersed within grains of said metal phase.

10

10. A zirconia based composite material as set forth in claim 7, wherein said ceramic phase has an average grain size of 2 μm or less.

15

11. A zirconia based composite material as set forth in claim 7, wherein said composite material comprises:

20

0.5 to 50 vol% of said metal phase, said metal phase contained in an amount equal to or less than the amount of said partially stabilized zirconia; said ceramic phase contained in an amount equal to or less than the amount of said metal phase; said metal phase and ceramic phase contained in amounts which total 60 vol% or less of said composite material.

25

12. A method of producing a zirconia based composite material
5 comprising the steps;

preparing a mixture of at least one first constituent
forming a partially stabilized zirconia including
1.5 to 4.5 mol% of yttrium oxide and at least one
second constituent forming a metal phase of at least
10 one metal element selected from the group consisting
of titanium, vanadium, niobium, tantalum, chromium,
molybdenum and tungsten; and

sintering said mixture in a non-oxidation atmosphere to
obtain said composite material which substantially
15 consists of said partially stabilized zirconia as a
matrix thereof and said metal phase dispersed in the
matrix.

20 13. A method as set forth in claim 12, wherein said mixture
further includes at least one third constituent forming a
ceramic phase of at least one ceramic selected from the group
consisting of Al_2O_3 , SiC, Si_3N_4 , B_4C , carbides, nitrides and
25 borides of titanium, vanadium, niobium, tantalum, chromium,
molybdenum and tungsten, thereby said composite material
substantially consisting of said partially stabilized zirconia

as the matrix and said metal phase and said ceramic phase which are dispersed in the matrix.

5

14. A method as set forth in claim 12, wherein said mixture is prepared by mixing a powder of said metal element having an average particle size of 1 μ m or less with a powder of said partially stabilized zirconia in such an amount that said
10 composite material contains 0.5 to 50 vol% of said metal phase and the amount of said metal phase is equal to or less than the amount of said partially stabilized zirconia.

15

15. A method as set forth in claim 12, wherein said mixture is prepared by mixing in a dry condition a powder of said partially stabilized zirconia with a powder of said metal element having an average particle size of 1 μ m or more.

20

16. A method as set forth in claim 12, wherein said mixture is prepared by milling a powder of said partially stabilized
25 zirconia the surface of which is coated with said metal element.

17. A method as set forth in claim 12, wherein said mixture is prepared by milling a granulated powder of said partially stabilized zirconia the surface of which is coated with said metal element.

18. A method as set forth in claim 13, wherein said mixture is prepared by mixing a powder of said partially stabilized zirconia with a powder of said metal element having an average grain size of 1 μ m or less and a powder of said ceramic having an average grain size of 1 μ m or less in such an amount that said composite material comprises:

0.5 to 50 vol% of said metal phase, said metal phase contained in an amount equal to or less than the amount of said partially stabilized zirconia; said ceramic phase contained in an amount equal to or less than the amount of said metal phase; said metal phase and ceramic phase contained in amounts which total 60 vol% or less of said composite material.

19. A method as set forth in claim 12, wherein said mixture is prepared by mixing an oxide of said metal element with a

powder of said partially stabilized zirconia, and said mixture is sintered in a reducing atmosphere.

5

20. A method as set forth in claim 12, wherein said mixture is prepared by mixing a hydride of said metal element with a powder of said partially stabilized zirconia, and then said
10 mixture is sintered in a reducing atmosphere.

21. A method as set forth in claim 19 or 20, wherein said
15 mixture is milled in a dry condition into a fine mixture powder prior to the sintering in said reducing atmosphere.

20 22. A method as set forth in claim 12, wherein said mixture is prepared by mixing a powder of said partially stabilized zirconia as said first constituent with an aqueous solution of a salt of said metal element as said second constituent, adding an alkali aqueous solution to a resultant to obtain a
25 precipitate, drying and heating said precipitate in an oxidation atmosphere to obtain a crystallized oxide powder of said precipitate, and said mixture is sintered in a reducing

atmosphere.

5 23. A method as set forth in claim 13, wherein said mixture is prepared by mixing a powder of said partially stabilized zirconia as said first constituent with an aqueous solution of a salt of said metal element as said second constituent, and an aqueous solution of an aluminum salt as said third
10 constituent, adding an alkali aqueous solution to a resultant to generate a precipitate, drying and heating said precipitate in an oxidation atmosphere to obtain a crystallized oxide powder of said precipitate, and said mixture is sintered in a reducing atmosphere.

15

24. A method as set forth in claim 12, wherein said mixture is prepared by mixing a first aqueous solution including a
20 zirconium salt and a yttrium salt as said first constituent with a second aqueous solution of a salt of said metal element as said second constituent, adding an alkali aqueous solution to a resultant to generate a precipitate, drying and heating said precipitate in an oxidation atmosphere to obtain a
25 crystallized oxide powder of said precipitate, and said mixture is sintered in a reducing atmosphere, the concentration of said yttrium salt in said first aqueous

solution is determined in such an amount that yttrium oxide is contained in an amount of 1.5 to 4.5 mol% relative to zirconia to form said partially stabilized zirconia in said composite material.

5

25. A method as set forth in claim 13, wherein said mixture is prepared by mixing a first aqueous solution including a zirconium salt and a yttrium salt as said first constituent with a second aqueous solution of a salt of said metal element as said second constituent, and a third aqueous solution of an aluminum salt as said third constituent, adding an alkali aqueous solution to a resultant to generate a precipitate, drying and heating said precipitate in an oxidation atmosphere to obtain a crystallized oxide powder of said precipitate, and said mixture is sintered in a reducing atmosphere, the concentration of said yttrium salt in said first aqueous solution is determined in such an amount that yttrium oxide is contained in an amount of 1.5 to 4.5 mol% relative to zirconia to form said partially stabilized zirconia in said composite material.

25

26. A method as set forth in claim 12, wherein said mixture is

prepared by mixing an aqueous solution including a zirconium salt and a yttrium salt as said first constituent with an organic solution of an alkoxide of said metal element as the second constituent, thereby hydrolyzing said alkoxide, adding
5 an alkali aqueous solution to a resultant to generate a precipitate, drying and heating said precipitate in an oxidation atmosphere to obtain a crystallized oxide powder of said precipitate, and said mixture is sintered in a reducing atmosphere, the concentration of said yttrium salt in said
10 aqueous solution is determined in such an amount that yttrium oxide is contained in an amount of 1.5 to 4.5 mol% relative to zirconia to form said partially stabilized zirconia in said composite material.

15

27. A method as set forth in claim 13, wherein said mixture is prepared by mixing a first aqueous solution including a zirconium salt and a yttrium salt as said first constituent
20 with an organic solution of an alkoxide of said metal element as said second constituent and a second aqueous solution of an aluminum salt as said third constituent, thereby hydrolyzing said alkoxide, adding an alkali aqueous solution to a resultant to generate a precipitate, drying and heating said
25 precipitate in an oxidation atmosphere to obtain a crystallized oxide powder of said precipitate, and said mixture is sintered in a reducing atmosphere, the

concentration of said yttrium salt in said first aqueous solution is determined in such an amount that yttrium oxide is contained in an amount of 1.5 to 4.5 mol% relative to zirconia to form said partially stabilized zirconia in said composite material.

28. A method as set forth in claim 13, wherein said mixture is prepared by mixing an aqueous solution including a zirconium salt and a yttrium salt as said first constituent with a first organic solution of an alkoxide of said metal element as said second constituent and a second organic solution of an aluminum alkoxide as said third constituent, thereby hydrolyzing the alkoxide of said metal element and said aluminum alkoxide, adding an alkali aqueous solution to a resultant to generate a precipitate, drying and heating said precipitate in an oxidation atmosphere to obtain a crystallized oxide powder of said precipitate, and said mixture is sintered in a reducing atmosphere, the concentration of said yttrium salt in said aqueous solution is determined in such an amount that yttrium oxide is contained in an amount of 1.5 to 4.5 mol% relative to zirconia to form said partially stabilized zirconia in said composite material.

29. A method as set forth in claim 12, wherein said mixture is prepared by mixing a powder of said partially stabilized zirconia as said first constituent with an organic solution of an alkoxide of said metal element as said second constituent, hydrolyzing a resultant to generate a precipitate, drying and heating said precipitate in an oxidation atmosphere to obtain a crystallized oxide powder of said precipitate, and said mixture is sintered in a reducing atmosphere.

10

30. A method as set forth in claim 13, wherein said mixture is obtained by mixing a powder of said partially stabilized zirconia as said first constituent with an organic solution of an alkoxide of said metal element as said second constituent and an organic solution of an aluminum alkoxide as said third constituent, hydrolyzing a resultant to generate a precipitate, drying and heating said precipitate in an oxidation atmosphere to obtain a crystallized oxide powder of said precipitate, and said mixture is sintered in a reducing atmosphere.

20

31. A method as set forth in claim 12, wherein said mixture is prepared by mixing a first organic solution including a zirconium alkoxide and a yttrium alkoxide as said first

25

constituent with a second organic solution of an alkoxide of said metal element as said second constituent, hydrolyzing a resultant to generate a precipitate, drying and heating said precipitate in an oxidation atmosphere to obtain a
5 crystallized oxide powder of said precipitate, and said mixture is sintered in a reducing atmosphere, the concentration of said yttrium alkoxide in said first organic solution is determined in such an amount that yttrium oxide is contained in an amount of 1.5 to 4.5 mol% relative to zirconia
10 to form said partially stabilized zirconia in said composite material.

15 32. A method as set forth in claim 13, wherein said mixture is prepared by mixing a first organic solution of a zirconium alkoxide and a yttrium alkoxide as said first constituent with a second organic solution of an alkoxide of said metal element as said second constituent and a third organic solution of an
20 aluminum alkoxide as said third constituent, hydrolyzing a resultant to generate a precipitate, drying and heating said precipitate in an oxidation atmosphere to obtain a crystallized powder of said precipitate, and said mixture is sintered in a reducing atmosphere, the concentration of said
25 yttrium alkoxide in said first organic solution is determined in such an amount that yttrium oxide is contained in an amount of 1.5 to 4.5 mol% relative to zirconia to form said partially

stabilized zirconia in said composite material.

5 33. A method as set forth in claim 12, wherein said mixture is prepared by mixing a powder of said partially stabilized zirconia with an oxide of said metal element, heating a resultant in an oxidation atmosphere to form an oxide powder including a complex oxide of said partially stabilized
10 zirconia and said metal element, and said mixture is sintered in a reducing atmosphere.

15 34. A method as set forth in claim 12, wherein said mixture is prepared by mixing a powder of said partially stabilized zirconia with said metal element, heating a resultant in an oxidation atmosphere to form an oxide powder including a complex oxide of said partially stabilized zirconia and said
20 metal element, and said mixture is sintered in a reducing atmosphere.

25 35. A method as set forth in claim 33 or 34, wherein the resultant is heated at a temperature of about 500°C to 1200°C in the air.

36. A method as set forth in any one of claims 16, 17, 19, 20, 22, 24, 26, 29, 31, 33, 34, wherein said mixture further includes at least one third constituent forming a ceramic phase of at least one ceramic selected from the group consisting of Al_2O_3 , SiC , Si_3N_4 , B_4C , carbides, nitrides and borides of titanium, vanadium, niobium, tantalum, chromium, molybdenum and tungsten.

10

37. A zirconia based composite material substantially as described in any of the Examples.

15

38. A method for making a zirconia based composite material substantially as described in any of the examples.

20

39. Use in a zirconia based composite material of a dispersed metal phase to toughen the material.

40. Use in a zirconia based composite material of a dispersed metal phase to strengthen the material.

Patents Act 1977
Examiner's report to the Comptroller under Section 17
(The Search report)

Application number
GB 9319405.8

Relevant Technical Fields

Search Examiner
MISS M M KELMAN

(i) UK Cl (Ed.M) C1J, C7A

(ii) Int Cl (Ed.5) C04B 35/00, 35/48; C22C 29/00, 29/12, 32/00

Date of completion of Search
11 NOVEMBER 1993

Databases (see below)

(i) UK Patent Office collections of GB, EP, WO and US patent specifications.

Documents considered relevant following a search in respect of Claims :-
1-38

(ii) ONLINE DATABASES: WPI

Categories of documents

- | | |
|---|---|
| X: Document indicating lack of novelty or of inventive step. | P: Document published on or after the declared priority date but before the filing date of the present application. |
| Y: Document indicating lack of inventive step if combined with one or more other documents of the same category. | E: Patent document published on or after, but with priority date earlier than, the filing date of the present application. |
| A: Document indicating technological background and/or state of the art. | &: Member of the same patent family; corresponding document. |

Category	Identity of document and relevant passages	Relevant to claim(s)
X	GB 1295413 A (METALLWERK PLANSEE)	1, 3, 12
X	GB 1109368 A (METALLWERK PLANSEE)	1, 2, 4, 5, 12
X	GB 1105646 A (METALLWERK PLANSEE)	1, 2, 4, 5, 12

Databases: The UK Patent Office database comprises classified collections of GB, EP, WO and US patent specifications as outlined periodically in the Official Journal (Patents). The on-line databases considered for search are also listed periodically in the Official Journal (Patents).

